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Version of attached file:

Published Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Prytulak, J. and Sossi, P.A. and Halliday, A.N. and Plank, T. and Savage, P.S. and Woodhead, J.D. (2016) 'Stable vanadium isotopes as a redox proxy in magmatic systems?', *Geochemical perspectives letters.*, 3 (1). pp. 75-84.

Further information on publisher's website:

<https://doi.org/10.7185/geochemlet.1708>

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■ Stable vanadium isotopes as a redox proxy in magmatic systems?

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P.S. Savage⁵, J.D. Woodhead⁶

Abstract

Recycling pathways of multivalent elements, that impact our understanding of diverse geological processes from ore formation to the rise of atmospheric oxygen, depend critically on the spatial and temporal variation of oxygen fugacity (fO_2) in the Earth's interior. Despite its importance, there is currently no consensus on the relative fO_2 of the mantle source of mid-ocean ridge basalts compared to the sub-arc mantle, regions central to the mediation of crust-mantle mass balances. Here we present the first stable vanadium isotope measurements of arc lavas, complemented by non-arc lavas and two co-genetic suites of fractionating magmas, to explore the potential of V isotopes as a redox proxy. Vanadium isotopic compositions of arc and non-arc magmas with similar MgO overlap with one another. However, V isotopes display strikingly large, systematic variations of ~2‰ during magmatic differentiation in both arc and non-arc settings. Calculated bulk V Rayleigh fractionation factors ($1000 \ln \alpha_{\text{min-melt}}$ of -0.4 to -0.5‰) are similar regardless of the oxidation state of the evolving magmatic system, which implies that V isotope fractionation is most influenced by differences in bonding environment between minerals and melt rather than changes in redox conditions. Thus, although subtle fO_2 effects may be present, V isotopes are not a direct proxy for oxygen fugacity in magmatic systems.

Received 29 July 2016 | Accepted 3 October 2016 | Published 26 October 2016

Introduction

Oxygen fugacity (fO_2), the chemical potential of oxygen, varies over ten orders of magnitude in igneous systems (Carmichael, 1991). Knowledge of mantle fO_2 is of critical importance for understanding the speciation of fluids in subduction zones and thus the efficiency of elemental transfer from slab to surface. Oxygen

fugacity is often reported in log units relative to a buffer reaction, commonly fayalite-magnetite-quartz (FMQ). Early study of mantle fO_2 employed oxygen thermobarometry, proposing that subduction zone magmas and their sources are more oxidised ($>FMQ +1$) than those found at mid-ocean ridges ($\sim FMQ$) (e.g., see review of Frost and McCammon, 2008).

However, the association of mantle fO_2 with tectonic setting has become contested following the introduction of novel approaches to its determination. The development of new proxies based on ratios of redox to non-redox sensitive elements, such as V/Sc and Fe/Zn, coupled with synthesis of global chemical databases such as GEOROC (<http://georoc.mpch-mainz.gwdg.de/georoc/>) and PETDB (<http://www.earthchem.org/petdb>), has led to the counterintuitive proposal that there is no difference in fO_2 between the mantle sources of arc and MORB lavas (Lee *et al.*, 2005, 2010). Despite this hypothesis, there is a consensus that basaltic melts found in arcs are more oxidised than their MORB counterparts, given, for example, their elevated $Fe^{3+}/\Sigma Fe$ ratios measured in melt inclusions (e.g., Kelley and Cottrell, 2009). In order to explain how oxidised arc basalts and more reduced MORBs can be derived from sources with similar fO_2 , processes subsequent to magma generation such as degassing and crystal fractionation have been invoked (e.g., Mallmann and O'Neill, 2009; Lee *et al.*, 2010). Evidence gleaned from both experimental and natural suites is conflicting, with cases of $Fe^{3+}/\Sigma Fe$ increasing, decreasing and remaining invariant during magmatic degassing and crystallisation (e.g., Brounce *et al.*, 2014; Waters and Lange, 2016). Thus lingering uncertainty as to whether the elevated $Fe^{3+}/\Sigma Fe$ in arc lavas is derived from their sources or during differentiation fuels continued debate.

The stable isotope composition of multivalent elements is theoretically linked to fO_2 . High temperature fractionation of stable isotopes is dictated by the vibrational frequencies of chemical bonds, with higher frequencies having larger bond force constants (K) and preferring heavier isotopes. An instructive estimate of the force constant is given by the mean bond strength: the quotient of average valence and co-ordination number (Pauling, 1929). Thus, atoms associated with higher oxidation state and/or lower co-ordination should, on average, incorporate a greater proportion of heavier isotopes. Therefore the possibility of resolving transition metal stable isotope variations in high temperature settings has the potential to define mantle fO_2 more clearly. Although it is tempting to employ simple comparative geochemistry (*i.e.* heavier isotope compositions equate to more oxidising conditions), the interplay between co-ordination environment and valence state is vital to interpreting the effect of changing fO_2 on isotope fractionation.

Vanadium as a Redox Proxy

Vanadium is a moderately incompatible, refractory multivalent (2+, 3+, 4+, 5+) element and the strong dependence of its partitioning behaviour on fO_2 is well-established (e.g., Canil, 1997; Toplis and Corgne, 2002; Mallmann and O'Neill, 2009). In all major mantle phases, vanadium becomes more incompatible with

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increasing fO_2 , leading to the application of V as a redox proxy (e.g., Shervais, 1982; Canil, 1997; Lee *et al.*, 2005; Mallmann and O'Neill, 2009). However, using concentrations alone results in fO_2 uncertainties on the order of 1–2 log units due to variations in degree of melting, original source concentration, and fractionating mineral assemblages (Lee *et al.*, 2003).

Vanadium has two stable isotopes, ^{51}V and ^{50}V . Their ratio is reported as per mille deviations, $\delta^{51}\text{V}$, relative to the AA (Alfa Aesar) V solution standard, defined as 0‰ (see Nielsen *et al.*, 2011). The extreme natural $^{51}\text{V}/^{50}\text{V}$ ratio of ~420 coupled with isobaric interferences from ^{50}Cr and ^{50}Ti on the minor ^{50}V isotope have historically prevented analyses to a precision useful for high temperature applications. These obstacles were recently overcome, and the first analytical protocol to determine $\delta^{51}\text{V}$ to a precision better than $\pm 0.15\text{‰}$ 2sd (Nielsen *et al.*, 2011; Prytulak *et al.*, 2011) demonstrated resolvable variations in igneous rocks of different silica content ($\delta^{51}\text{V}_{\text{basalts}} < \delta^{51}\text{V}_{\text{andesites}}$). We present the first $\delta^{51}\text{V}$ measurements directly exploring the potential of $\delta^{51}\text{V}$ as a redox proxy in magmatic systems. Specifically, we investigate the effect of magmatic evolution and determine if a resolvable $\delta^{51}\text{V}$ difference exists between arc and non-arc lavas.

Methods

The oxygen fugacity of the two tectonic settings investigated herein (Mariana arc and Hekla, Iceland) have been previously determined by two independent means: by way of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios that are converted to fO_2 , and by Fe–Ti oxybarometry. Both methods indicate that Mariana arc basalts are generally ~1–2 log units more oxidised compared to Icelandic basalts from Hekla (e.g., de Moor *et al.*, 2005; Moune *et al.*, 2007; Brounce *et al.*, 2014; Shorttle *et al.*, 2015). We chose forty whole rock samples from three well-studied lava suites: 1) primitive arc lavas of the Mariana Central Island Province (CIP; Elliott *et al.*, 1997), 2) co-genetic lavas from Anatahan volcano in the Mariana arc (Wade *et al.*, 2005) and 3) co-genetic lavas from Hekla volcano, Iceland (Savage *et al.*, 2011). Published major, trace and isotopic data are found in Table S-1.

Chemical separation and V isotope measurements were made at Oxford University and Imperial College London, following Nielsen *et al.* (2011). Description of methods and isotopic data are found in the Supplementary Information and Table S-2.

Results and Discussion

Two key observations arise from Figure 1. First, there is a striking range of ~2‰ towards heavy $\delta^{51}\text{V}$ with progressive differentiation in both suites of lavas, which is an order of magnitude larger than Fe isotope variations in fractionating magmas (e.g., Schuessler *et al.*, 2009; Sossi *et al.*, 2012). Second, basaltic lavas from the Marianas, Iceland and MORB have overlapping $\delta^{51}\text{V}$.

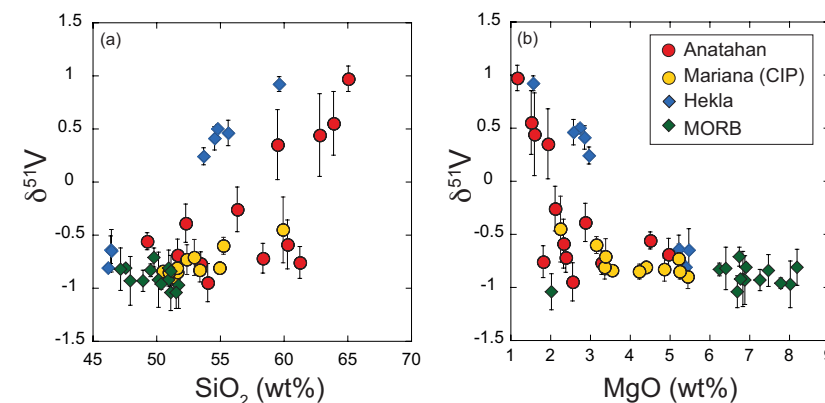


Figure 1 $\delta^{51}\text{V}$ variations with SiO_2 (a) and MgO (b). CIP = Central Island Province. MORB data from Prytulak *et al.* (2013). Uncertainties on isotope measurements are external 2 sd.

The remarkable magnitude of high temperature $\delta^{51}\text{V}$ fractionation towards heavy values with magmatic evolution is unlikely to be due to the difference in calculated fO_2 between Hekla and the Marianas, because the $\delta^{51}\text{V}$ variation is similar for both suites. Instead, the primary control on isotope fractionation appears to be differences in mineral–melt bonding environment. Oxide minerals such as (titano)magnetite host the majority of V in magmatic systems. Trivalent vanadium is preferentially incorporated in the VI-fold sites of (titano)magnetite, the thermodynamically stable configuration (O'Neill and Navrotsky, 1984) resulting from its high octahedral site preference energy. Vanadium's oxidation and co-ordination in silicate melts is not constrained by stoichiometry, but is always higher and lower, respectively, than in co-existing (titano)magnetite (Righter *et al.*, 2006). Thus (titano)magnetite (and other ferromagnesian minerals) should be isotopically light, and crystallisation will lead to a progressively heavier residual melt. A significant departure to heavy $\delta^{51}\text{V}$ is observed at ~60 wt. % SiO_2 at Anatahan, and ~55 wt. % at Hekla, although petrographic and chemical evidence demonstrates oxide fractionation occurring earlier in both suites. Indeed, significant (titano)magnetite crystallisation and removal is necessary to impact $\delta^{51}\text{V}$ signatures whilst melt V concentration is relatively high. We speculate that magma chamber processes at Anatahan, where lavas are generally more evolved, are responsible for the lighter and more variable $\delta^{51}\text{V}$ in lavas with between 2 and 4 wt. % MgO compared to Hekla (Fig. 1b).

Self-consistent models of fractional crystallisation of cotectic phases have been constructed to account for systematic variations in major and trace element concentrations, as well as isotopic compositions in Hekla and Anatahan lavas (Fig. 2). Input parameters and results are provided in the Supplementary Information (Table S-3). Given the strong dependence of V partitioning on fO_2 ,



it is of particular interest to assess how the partition coefficient of V in (titano) magnetite differs between the two suites. A D^{mag}_V of 32 ± 4 is calculated from analyses of Anatahan lavas (de Moor *et al.*, 2005), a value that reproduces major, trace and isotopic trends very well. The required D^{mag}_V for Hekla lavas, however, must be significantly higher (~ 42) to reproduce the data. The relative difference in D^{mag}_V between the two suites is consistent with lower fO_2 at Hekla than Anatahan (*e.g.*, Toplis and Corgne, 2002). The same input parameters are used to perform Rayleigh calculations to estimate the bulk V isotope fractionation factor (Fig. 3). Both suites require large $\Delta^{51}V_{\text{min-melt}}$ fractionation factors on the order of $1000\ln\alpha_{\text{min-melt}}$ of -0.4 to -0.5‰ . Arguably, a larger fractionation factor is required for Anatahan versus Hekla, however, the effect is subtle and difficult to resolve confidently within the current analytical precision.

Clearly, differences in mineral-melt bonding environment are key to producing large $\delta^{51}V$ fractionations. However, prior to significant (titano) magnetite crystallisation, $\delta^{51}V$ is identical within uncertainties in arc lavas, Icelandic lavas and MORB at similar MgO contents (Fig. 1). If interpreted as a direct fO_2 proxy, this conflicts with oxybarometry in peridotites, but is notionally consistent with their similar V/Sc ratios. This conclusion hinges, however, upon the assumption of a homogeneous source, both with respect to V/Sc and $\delta^{51}V$, an assumption that may be violated. For instance, $\delta^{51}V$ becomes isotopically lighter in progressively depleted (clinopyroxene-poor) peridotites (Prytulak *et al.*, 2013). This is an important observation because the arc mantle wedge has been inferred

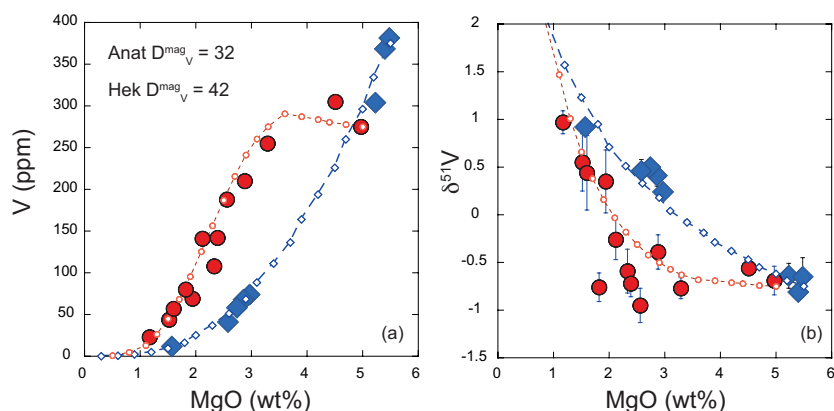


Figure 2 Cotectic fractional crystallisation models. Each small symbol represents a 5% crystal fractionation increment. See Supplementary Information for input parameters. Symbols and uncertainties as in Figure 1.

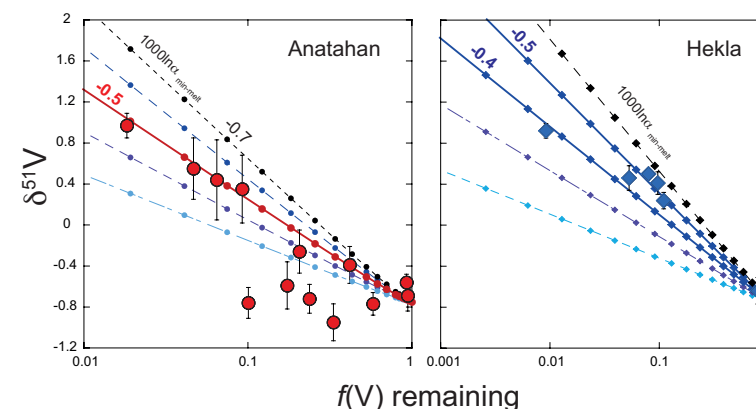


Figure 3 Rayleigh fractionation calculations with same parameters as Figure 2. Symbols and uncertainties as in Figure 1.

to be markedly depleted (*e.g.*, Woodhead, 1993; Nebel *et al.*, 2015) with respect to the source of MORB. In the absence of a common source, observations of similar V/Sc and $\delta^{51}V$ must be explained.

Primary arc magmas are notoriously rare, thus most information is garnered from basaltic andesites with Mg# too low (~ 0.5 assuming 20% Fe^{3+}) to be in equilibrium with normal mantle (~ 0.9). Isotope fractionation during partial melting is possible, although high temperatures should minimise the effect. It is, however, perplexing that the well-constrained $\delta^{51}V_{\text{MORB}}$ is isotopically lighter than most peridotites and the bulk silicate Earth ($\delta^{51}V_{\text{MORB}} = -0.95 \pm 0.13\text{‰}$; $\delta^{51}V_{\text{BSE}} = -0.7 \pm 0.2\text{‰}$; Prytulak *et al.*, 2013). The peridotite trend towards lighter $\delta^{51}V$ with progressive depletion thus negates a simple explanation of isotope fractionation during melt extraction (Prytulak *et al.*, 2013). Given the strong effect of mineral-melt fractionation on $\delta^{51}V$, the potential for early phases to change the $\delta^{51}V$ of arc basalts should be considered. Water-rich magmas crystallise Cr-rich spinel before olivine (Feig *et al.*, 2010), potentially scavenging V. Oxide fractionation will drive remaining liquid to heavier $\delta^{51}V$, making early spinel crystallisation a viable mechanism to increase $\delta^{51}V$ in arc magmas. If arc magmas are derived from a depleted source with a lighter initial V isotope composition than the MORB source, it is therefore possible that the competing effects of source depletion and Cr-spinel fractionation result in similar $\delta^{51}V$ in mafic arc and non-arc magmas. Mineral separate data and the analysis of more primitive magmas are required to investigate this premise since it is currently not possible to evaluate the magnitude of isotopic increase due to early Cr-rich spinel, and/or partial melting, as there are no combined V concentration and $\delta^{51}V$ on spinel and scant peridotite whole rock data.

If arc magmas are derived from mantle more depleted than MORB, their sources should have lower $\delta^{51}V$ and V/Sc. The decrease of V/Sc in the source



will be exacerbated if prior melt-depletion occurs at high fO_2 . Therefore, the observation of similar $\delta^{51}V$ and V/Sc ratios in high MgO lavas from both settings can be interpreted as evidence of melting of more depleted, oxidised sources in arcs. This concept is illustrated with two hypothetical sources in Figure 4a, with examples of simple forward trace element modal (Fig. 4b) and non-modal (Fig. 4c) melting models comparing V/Sc in lavas derived from these two sources. Overall, the effect of source depletion (*i.e.* less V) coupled with higher fO_2 (and thus lower D_V), can offset a more fertile (*i.e.* more V) less oxidised (higher D_V) source to yield similar V/Sc in resulting melts. Thus the confluence of $\delta^{51}V$ and V/Sc in arc and MORB lavas may paradoxically require differences in their source fO_2 . Clearly, there are many possible solutions to such models, and the absolute values of V/Sc are very sensitive to input parameters (see Supplementary Information), however, given the assumption of a more oxidised, depleted arc source, the similarity of V/Sc in arc lavas and MORB at 10–15 % melt is relatively straightforward to reproduce.

Irrespective of the trade-offs involved in interpretation of relative oxidation states of arc and non-arc lavas, Rayleigh fractionation of oxide phases is dominantly responsible for the magnitude of observed V isotope fractionation in differentiating magmatic suites. Subtle fO_2 -related variations are perhaps

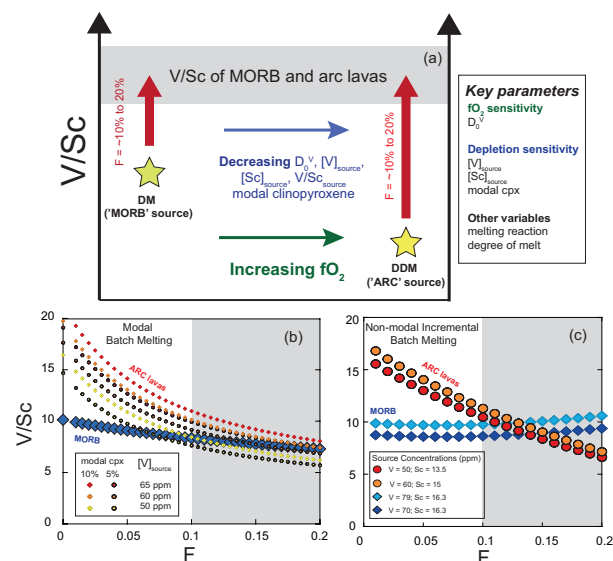


Figure 4 (a) Conceptual effect of depletion and oxidation on V/Sc ratios from two hypothetical spinel peridotite sources. (b,c) Modal and non-modal melting models for the sources in (a). Grey fields highlight reasonable melting degrees. Partition coefficients, modal compositions and melting reactions are detailed in the Supplementary Information. DM = depleted mantle, DDM = depleted MORB mantle, F = melt fraction.

overprinted onto first order bonding-environment induced fractionations, but these require a much richer understanding of $\delta^{51}V$ variations during magmatic processes to be applicable. Therefore, elemental partitioning of V yields a more direct relationship with fO_2 than the current understanding of V isotopes at high temperatures permits.

Acknowledgements

JP was funded by NERC postdoctoral fellowship NE/H01313X/2, with support of the Oxford laboratories from an Advanced ERC grant (NEWISOTOPEGEOSCIENCE) to ANH. PAS by an APA PhD scholarship and ANU Vice-Chancellor's Scholarship. We appreciate thoughtful reviews by F. Poitrasson and G. Mallmann. Tim Elliott is thanked for providing CIP samples. Although he may not necessarily agree with all the ideas presented, we thank Hugh O'Neill for many formative discussions.

Editor: Bruce Watson

Additional Information

Supplementary Information accompanies this letter at www.geochemical-perspectivesletters.org/article1708



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